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高氧还原活性热解碳载钴聚吡咯研究

High Activity toward Oxygen Reduction Reaction and
Pyrolyzed Carbon Supported Cobalt Polypyrrole

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High Activity toward Oxygen Reduction Reaction and Pyrolyzed Carbon Supported Cobalt Polypyrrole



A Thesis Submitted for the Degree of Master of
Engineering at Xiamen University

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摘要

催化剂是燃料电池正常运行的关键材料之一，以铂为主的贵金属催化剂价格昂贵，严重制约了低温燃料电池的商业化；阴极氧还原反应过电位较大，极大地限制了燃料电池的性能和寿命。因此，研究和开发价格低廉、高活性和高稳定性的非铂阴极催化剂成为近年来催化剂研究的主要方向。碳载钴聚吡咯催化剂具有良好的稳定性，但催化活性相对较低。为了获得高氧还原活性，本论文以乙酸钴为钴源，聚吡咯为氮源，商用炭黑为碳载体制备碳载钴聚吡咯催化剂，深入探讨了钴载量、氮碳比、掺杂剂种类与数量以及热处理时间等对催化活性的影响，并重点考察了掺杂剂中硫元素的引入对催化剂氮含量、孔径分布和碳载体石墨化程度的影响。通过设计正交试验，优化了合成参数，制备出高催化活性的热解碳载钴聚吡咯阴极催化剂。

结果发现，分别引入十二烷基苯磺酸钠、对甲苯磺酸钠及苯磺酸钠三种掺杂剂，催化剂的转移电子数均由未掺杂的 2.7 提高到 3.1。同时，掺杂剂的引入降低了催化剂的微孔面积，但延长热处理时间可以提高催化剂的微孔面积。由于掺杂剂中含有的硫元素与碳结构的相互作用，不仅增加了催化剂中的氮含量，而且提高了碳载体的石墨化程度，其中苯磺酸钠掺杂的催化剂氧还原活性最好，氮含量增加了 31%，碳载体石墨化程度提高了 8.71%，微孔面积仅减少 4.70%。

通过正交试验得到的催化剂最佳合成参数为：钴载量为 5%，氮碳质量比为 3 : 1，苯磺酸钠与吡咯的摩尔比为 1 : 2，热处理时间为 10h。由此制备的热解碳载钴聚吡咯催化剂的氧还原峰电位为 600mV，转移电子数为 3.6，氮含量高达 3.994%。合成参数中热处理时间对催化活性影响最大，延长热处理时间有利于提高活性。此外，催化剂的氮含量也显著影响活性，适当增加氮碳比可以增加氮含量，但延长热处理时间则会减少氮含量。热解碳载钴聚吡咯催化剂中检测出钴氧化物。进一步的分析表明，催化剂表面钴氧化物的生成，有利于催化过氧化氢的分解，实现四电子氧还原过程。但催化剂体相钴氧化物的生成则导致催化剂活性减弱。因此，选择合适的钴载量是获得高氧还原活性的热解碳载钴聚吡咯催化剂的重要基础。

关键词：燃料电池 氧还原反应 阴极催化剂 碳载钴聚吡咯 掺杂剂

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Abstract

Catalysts are one of the key materials during the operation of fuel cells. The commercialization of low temperature fuel cells has been greatly limited due to the use of expensive platinum based catalysts. Large overpotentials required for oxygen reduction reaction (ORR) at cathode have restricted the performance and durability of fuel cells. It has, therefore, become the main research direction in catalysts to research and develop cathode catalysts with low cost, high activity and high stability. Carbon supported cobalt polypyrrole (Co-PPy/C) exhibited good stability, but relatively low catalytic activity. In order to achieve higher activity toward ORR, this work was conducted to prepare Co-PPy/C by using cobalt acetate as a cobalt source, polypyrrole as a nitrogen source, and commercially available carbon black as a support. Effects of cobalt load, ratio of nitrogen to carbon, the type and amount of dopants and heat treatment time on catalytic activity were extensively investigated; in particular, effects of sulfur element introduced from dopants on nitrogen content, pore distribution and the degree of graphitization in carbon support were examined. Through the designed orthogonal tests, the pyrolyzed Co-PPy/C cathode catalysts with high catalytic activity were obtained under the optimized synthetic conditions.

It was found that the transfer electron numbers of the doped catalysts were increased to 3.1 from 2.7 of the non-doped catalyst by the introduction of three different dopants, namely, sodium dodecylbenzene sulfonate (DBSNa), sodium paratoluene sulfonate (TSNa), and sodium benzenesulfonate (BSNa). The areas of micropores in catalysts were simultaneously reduced by introducing dopants, however, could be improved by extending heat treatment time. The interactions between sulfur element and carbon structure increased not only the nitrogen contents, but also the degree of graphitization in carbon supports. The BSNa doped catalyst showed the best ORR activity. The nitrogen content increased 37%, the degree of graphitization improved 8.71% and the areas of micropores reduced only 4.7%.

Through the orthogonal tests, the optimized synthetic parameters were determined to be 5% of the cobalt load, 3:1 for the weight ratio of pyrrole to carbon, 1:2 for the molar ratio of BSNa to pyrrole and 10h of the heat treatment time. The peak potential of ORR reached 600mV, and the transfer electron number was 3.6 with the nitrogen content as high as 3.994% for the catalyst prepared under the optimized synthetic conditions. The heat treatment time was found to be one of the most significantly influencing parameters on the catalytic activity which could be enhanced with the longer heat treatment time. In addition, the activity of catalysts was notably affected by nitrogen contents which could be higher by increasing the ratio of nitrogen to carbon but lower by extending the heat treatment time.

Cobalt oxides were identified in the pyrolyzed Co-PPy/C catalyst. Further analysis indicated that the formation of cobalt oxides at the surface of catalyst was beneficial to catalyze the decomposition of hydrogen peroxide and to realize a 4-electron reaction path. However, the formation of cobalt oxides in the bulk of catalyst was detrimental to activity of the catalyst. It is, therefore, very important to choose a suitable amount of cobalt when preparing pyrolyzed Co-PPy/C in an effort to achieve high activity toward ORR.

Key words: fuel cells; oxygen reduction reaction; cathode catalyst; carbon supported cobalt polypyrrole; dopant

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